

The Synthesis and Characterization of Pu(VII)

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High-valent actinide ions provide information about bonding and f-hybridization that is unavailable elsewhere on the periodic table. Whereas high-valent ions across much of the periodic table have been well characterized, there has been relatively little work done on the synthesis and characterization of samples containing transuranic ions. High-valent transuranic ions are very unstable and exist for very short times only in very strongly basic solutions. In addition, these radioactive ions have very complex chemistry that includes radiolysis and disproportionation reactions. These combined difficulties have proven insurmountable until our recent successful efforts to synthesize and characterize Pu(VII) in solution. Whereas Pu(VII) has been previously reported in the literature, questions about its existence have persisted, and no structural characterization has been reported. We have utilized our unique combination of hot laboratory facilities in the Chemistry division, staff with expertise in actinide chemistry, the Actinide Facility, and the BESSRC CAT at the APS to attack this longstanding problem. A freshly prepared Pu(VI) sample in strongly basic solution was transported to the APS where it was converted to Pu(VII), via ozonolysis, while simultaneously collecting X-ray absorption data on beam line 12-BM-B. The data clearly show the evolution of the dioxo coordination indicative of Pu(VI) and other higher valent actinides including U(VI), into an unusual tetraoxo-coordination environment. We have seen a similar coordination in our previous work with Np(VII), which was generated electrochemically in the synchrotron beam. A detailed analysis of the Pu(VII) coordination, combined with DFT calculations similar to those done on the Np analog are expected to bring a further understanding of the competition between the f- and d-orbitals for electron density. The Np(VII) and Pu(VII) coordination environments bridge the gap between the tetrahedral coordination seen in high-valent transition metals, such as MoO_4^{2-} and the dioxo coordination seen for hexavalent U, Np, and Pu.